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The reaction is conducted in the cold. It has been established that the first members of the series of phenylphosphonous esters react so vigorously that it is occasionally necessary to apply external cooling.

Certain experimental data on the obtained esters of phenyltrichloromethylphosphonic acid are presented in Table 1.

The first two esters of phenyltrichloromethylphosphonic acid obtained are in crystalline form; the third and fourth are colorless liquids having a characteristic odor.

Further, a study was made of the interaction of trichlorobromomethane and the ethyl ester of phenylphosphonous acid. The reaction itself is of a vigorous type followed by the evolution of ethyl bromide and formation of ethyl esters of phenyltrichloromethylphosphonic acid.

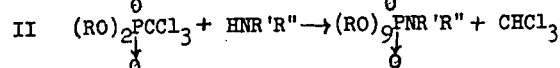
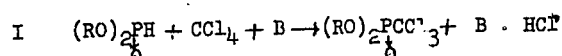
The reaction of the same initial ester with carbon tetrachloride is accompanied by extensive generation of heat, separation of ethyl bromide, and formation of a dark brown liquid of a heavy consistency which does not crystallize in a desiccator even if kept there for a long time. All attempts to subject this liquid to vacuum distillation have failed.

Numerous experiments set up to study the interaction of tetrachloroethane and perchloroethylene with esters of phenylphosphonous acid conducted under the same temperature conditions have failed to give any positive results.

Table 1

Formula	Temp (°C)	Bp at 1 mm (°C)	$d_4^{20}$	$n_D^{20}$	Yield (%)
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CCl}_3 \end{array} \text{P} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{OCH}_3$	108	Decomposes	--	--	61
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CCl}_3 \end{array} \text{P} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{OC}_2\text{H}_5$	79	147-148	--	--	66
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CCl}_3 \end{array} \text{P} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{OC}_3\text{H}_7\text{-n}$	--	150-152	1.3078	1.4945	70
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CCl}_3 \end{array} \text{P} \begin{array}{c} \diagup \\ \text{O} \end{array} \text{OC}_6\text{H}_{13}\text{iso}$	--	155-156	1.2861	1.4995	58

Recently, when most of the above study had been completed, it came to my knowledge that English chemists (2) had suggested a new method for the phosphorization of amines, namely treating dialkylphosphorous acids with carbon tetrachloride and the amine in question as follows:



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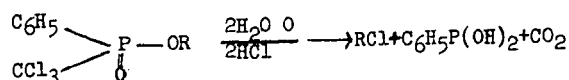
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As can be seen from the above, the esters of trichloromethylphosphonic acid appear as an intermediate product of the reaction. However, the authors have failed in their efforts to isolate these esters as an end product. The attempt to prepare these esters by direct action of carbon tetrachloride on triethylphosphite has failed as well.

The results of my research along this line have demonstrated that the reaction of triethylphosphite and other analogous esters of phosphorous acid with carbon tetrachloride takes place at increased temperatures under formation of alkyl esters of trichloromethylphosphonic acid, while the esters of phenylphosphonous acid react vigorously even at room temperature, accompanied by the formation of phenyltrichloromethylphosphonic acid esters.

My subsequent experiments on the action of amines (aniline or amylamine) on already formed esters of phenyltrichloromethylphosphonic acid led to the same end products obtained by the English chemists. Thus, according to results of my latest experiments, the interaction of carbon tetrachloride with diethylphosphorous acid in the presence of amines has been correctly interpreted by them.

When phenyltrichloromethylphosphonic acid esters are heated with concentrated hydrochloric acid, they saponify and evolve alkylchloride, carbon dioxide, and phenylphosphonous acid according to the following equation:



#### Experimental Part

The starting materials, i.e., the esters of phenylphosphonous acid, were obtained through the action of phenyldichlorophosphine on the corresponding alcohols in the presence of dimethylaniline. The basic physical constants of these esters are given in Table 2.

Table 2

<u>Formula</u>	<u>Bp at 10-13 mm (°C)</u>	<u>d<sub>4</sub><sup>20</sup></u>	<u>n<sub>D</sub><sup>20</sup></u>
$\text{C}_6\text{H}_5\text{P}(\text{OCH}_3)_2$	94-94.5	1.0972	1.5118
$\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2$	110-111	1.0405	1.5063
$\text{C}_6\text{H}_5\text{P}(\text{OC}_3\text{H}_7)_2\text{-n}$	132.5-133.5	1.0123	1.4939
$\text{C}_6\text{H}_5\text{P}(\text{OC}_4\text{H}_9)_2\text{-iso}$	144-145	1.0060	1.4658

#### Preparations of Phenylchloromethylphosphonic Acid Methyl Ester

Eighteen grams of carbon tetrachloride were placed in a flask equipped with a reflux condenser. Into the same flask were gradually added 20 g of phenylphosphonous acid methyl ester. The reaction was accompanied by generation of heat. After the entire quantity of phenylphosphonous acid methyl ester was put into the flask, the flask was heated for 3 hr in a hot-water bath. During this reaction, methylchloride was formed in quantity. After cooling, the obtained substance crystallized. These colorless crystals melted at a temperature of 108 deg. The yield was 61 per cent of the theoretical.

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0.1260 g of substance: 0.1974 g AgCl

0.1006 g of substance: 23.15 ml NaOH (1 ml NaOH = 0.4971 mg P)

Found (in %): Cl 38.76; P 11.45

$C_8H_8O_2Cl_3P$ . Calculated (in %): Cl 38.90; P 11.35

The substance is soluble in benzene, ether, dioxane, and alcohol.

Preparation of Phenyltrichloromethylphosphonic Acid Ethyl Ester

From 15 g of carbon tetrachloride and 19.2 g of phenylphosphonous acid ethyl ester was obtained the phenyltrichloromethylphosphonic acid ethyl ester. The reaction was accompanied by heat generation; external cooling was needed occasionally. Six or seven grams of ethyl chloride were formed, which is almost the theoretical quantity. The mass remaining in the flask was distilled in vacuum. The boiling point of the main fraction was 147-148 deg at 1 mm. The substance crystallized in the receiver. The melting point of the colorless crystals was 79 deg. The yield of the pure substance amounted to 18 g, or about 66 percent of the theoretical.

0.1554 g of substance: 0.2314 g AgCl

0.1266 g of substance: 28 ml NaOH  
(1 ml NaOH = 0.4791 mg P)

Found (in %): Cl 36.84; P 10.94

$C_9H_{10}O_2Cl_3$ . Calculated (in %): Cl 37.00; P 10.79

The phenyltrichloromethylphosphonic acid ethyl ester may be dissolved in a great number of organic solvents, and reacts with aniline and amylamine, generating heat and forming crystallized aminophosphates.

Preparation of Phenyltrichloromethylphosphonic Acid n-Propyl Ester

The interaction of 15 g of carbon tetrachloride with 21 g of phenylphosphonous acid n-propyl ester produced the phenyltrichloromethylphosphonic acid n-propyl ester. The propyl chloride was removed from the flask under normal pressure. The remaining liquid was subjected to vacuum distillation. The boiling point was found to be 150-152 deg at 1 mm. Yield of the substance was about 70 percent of the theoretical.

0.1240 g of substance: 26.3 ml NaOH (1 ml NaOH = 0.4971 mg P)  
Found (in %): P 10.54

$C_{10}H_{12}O_2Cl_3P$ . Calculated (in %): P 10.29

The ester a colorless liquid of heavy consistency, has a pleasant odor similar to chloroform.

$d_4^{20}$  1.3078;  $d_4^{14}$  1.2918;  $n_D^{19}$  1.4945

Preparation of Phenyltrichloromethylphosphonic Acid Isobutyl Ester

From 12 g of carbon tetrachloride and 20 g of phenylphosphonous acid was obtained the phenyltrichloromethylphosphonic acid isobutyl ester. A part of isobutyl chloride was removed under normal pressure and the remaining substance subjected to vacuum distillation. The boiling point was established at 155-156 deg, at 1 mm. The yield of the substance was 58 percent of the theoretical.

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0.1069 g of substance: 0.1454 g AgCl

0.1048 g of substance: 21.2 ml NaOH (1 ml NaOH = 0.4971 mg P)

0.1064 g of substance: 21.5 ml NaOH (1 ml NaOH = 0.4971 mg P)

Found (in %): Cl 33.65; P 10.05; 10.04

 $C_{11}H_{14}O_2Cl_3P$ . Calculated (in %): Cl 33.72; P 9.84

This ester, a colorless liquid, has a pleasant odor. It is soluble in a large number of organic solvents.

 $d_4^{20}$  1.2861;  $d_4^{13}$  1.2697;  $n_D^{18}$  1.4993Action of Trichlorobromomethane on Phenylphosphonous Acid Ethyl EsterThe trichlorobromomethane, prepared by the Paterno process, had the following physical constants: boiling point, 104 deg and  $d_4^{20}$  2.0551.

Ten and a half grams of trichlorobromomethane were placed in a flask equipped with a reflux condenser. To this substance were added, drop by drop, 10 g of phenylphosphonous acid ethyl ester. The first few drops caused a noticeable rise in temperature. To obtain a complete reaction, the substance in the flask was heated for an hour on a hot-water bath. Afterward it was subjected to distillation. Under normal pressure a fraction having a boiling point of 37-40 deg was obtained. Further distillation was conducted in vacuum. The main fraction boiled at 146-148 deg (at 1 mm) and crystallized in the receiver. The melting point of the crystals was 79 deg. The yield amounted to 11.5 g of substance, i.e., 79.6 percent of the theoretical.

A mixture of this substance and phenyltrichloromethylphosphonic acid ethyl ester had a melting point of 79 deg.

Action of Carbon Tetrabromide on Phenylphosphonous Acid Methyl Ester

Fifteen grams of carbon tetrabromide in 100 ml of absolute ether were placed in a flask. Under efficient cooling, a solution of 8.1 g of phenylphosphonous acid methyl ester in 50 ml of absolute ether was added by means of a dropping funnel. The reaction was of a vigorous type, accompanied by the formation of methyl bromide, which was collected. Almost 4.1 g of methyl bromide were formed. After the absolute ether had been removed, there remained in the flask a heavy dark brown liquid, which could not be vacuum distilled and did not crystallize even after considerable time.

Action of Carbon Tetrabromide on Phenylphosphonous Acid Ethyl Ester

The carbon tetrabromide was produced by the Wallach process. The melting point was 94 deg. Purification was by vacuum distillation. Sixteen and eight tenths g of carbon tetrabromide in 100 ml of absolute ether were placed in a flask equipped with a reflux condenser. Under exterior cooling, a solution of 10 g of phenylphosphonous acid ethyl ester in 60 ml of absolute ether was added through a dropping funnel. The reaction was accompanied by evolution of heat. When the entire quantity of phenylphosphonous acid ethyl ester was in the flask, the mass was stirred for an hour at room temperature and then left overnight [in the same flask]. On the following day, the ether and ethyl bromide were distilled off.

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The substance remaining in the flask, in the form of a heavy dark liquid, was put in a crystallizer. It did not crystallize, even after a considerable time, nor could it be vacuum distilled. The substance is unstable.

Saponification of Phenyltrichloromethylphosphonic Acid Methyl Ester

Five grams of phenyltrichloromethylphosphonic acid methyl ester and 15 ml of concentrated hydrochloric acid were put into a sealed tube and heated for 6 hr at a temperature of 120-130 deg. After cooling, the tube was opened, at which time considerable pressure was noticed. By repeated evaporation with water on a water bath, the volatile products of reaction and the hydrochloric acid were removed, whereupon the remaining substance crystallized. After recrystallization from alcohol, the substance melted at 158 deg and its other physical constants also corresponded to phenylphosphonous acid.

Conclusions

1. Through the reaction of carbon tetrachloride with phenylphosphonous acid esters, there were obtained and analyzed new compounds, namely various esters of phenyltrichloromethylphosphonic acid.
2. It was ascertained that trichlorobromomethane reacts with phenylphosphonous acid ethyl ester, yielding ethyl bromide and forming phenyltrichloromethylphosphonic acid ethyl ester.
3. It was also established that carbon tetrabromide reacts with phenylphosphonous acid esters, yielding alkyl bromide and forming a liquid of heavy consistency which cannot be distilled in vacuum.

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